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ELECTRON PARAMAGNETIC RESONANCE STUDY OF CHROMIUM⁺³ IN X-RAY IRRADIATED RUBY

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16. Abstract By EPR technique, dynamic measurements were made of the increase of Cr ⁺³ concentration in the X-ray irradiated ruby crystals during isothermal annealings. The thermal recovery of chromium ions to the +3 state was found to be a first-order process. The activation energy of this process was found to be 1.37±0.07 eV. The method described herein should be generally applicable to the study of decays involving paramagnetic centers.			
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SUMMARY

The ruby chromium⁺³ (Cr^{+3}) fine structure and relative intensity were determined at 9.543-gigahertz (GHz) excitation. The observed line positions of all transitions were in excellent agreement with those predicted from the energy levels calculation of J. Weber. Irradiation of ruby with X-rays at total doses greater than 10^6 roentgens caused a 27-percent decrease in Cr^{+3} concentration which is reversible by heating. By electron paramagnetic resonance (EPR) technique, we observed that the thermal recovery of the chromium ions to the +3 state was a first-order process. The activation energy of this process was found to be 1.37 ± 0.07 electron volts (eV).

INTRODUCTION

Many investigations have been made on ruby crystals, especially in recent years, when it has become the most commonly used laser material. A current research interest is the nature of the color centers responsible for the increased threshold of a ruby laser after long periods of operation. Irradiation with γ -rays has also been reported to cause similar increase in the generation threshold of the ruby laser (ref. 1). Arkhengelskii, Morgenshtern, and Neustruev (ref. 2) have shown that the characteristics of the centers arising from optical treatment and γ -ray irradiation are identical and that subsequent thermal decoloration is accompanied by luminescence in the R-line region. Forestieri and Grimes (ref. 3) have reported that irradiation of ruby preannealed in air results in a 20-percent loss of Cr^{+3} and the formation of Cr^{+4} and Cr^{+6} . Maruyama and Matsuda (ref. 4) have suggested the presence of Cr^{+2} as the origin of the four adsorption bands observed in γ -ray irradiated ruby.

More information on the radiation produced centers in ruby is still needed to establish a complete picture of the damage process. By EPR technique we have investigated

the relative Cr^{+3} concentration in single ruby crystals before and after X-ray irradiation as well as the related isothermal annealing kinetics of the color centers in the irradiated crystals. The aim was to add to establishing a radiation damage model for the ruby laser.

EXPERIMENTAL DETAILS AND RESULTS

The ruby crystals used were Linde laser quality with a 0.05 percent chromic oxide (Cr_2O_3) concentration. Their dimensions were 2 by 2 by 10 millimeters, with the c-axis either parallel or normal to the long dimension to within $\pm 2^\circ$. The EPR measurements were made at 9.543 ± 0.007 gigahertz, using a Varian 4500 spectrometer.

Ruby Cr^{+3} Fine Structure

The resonance fields for Cr^{+3} are a function of θ , the angle between the applied field and the c-axis of the ruby crystal. A plot of such a function was a prerequisite for the study planned. Results are given in figure 1, where the Cr^{+3} fine-structure line positions and intensities are plotted as a function of the polar angle θ . The present mapping represents an improvement over earlier works (refs. 3 and 5 to 7) on Cr^{+3} resonance in ruby crystal. The line positions of all transitions observed are in excellent agreement with those predicted from the ruby Cr^{+3} energy-level calculations of Weber (ref. 8). As an illustration, figure 2 depicts the calculated energy levels of Cr^{+3} in ruby

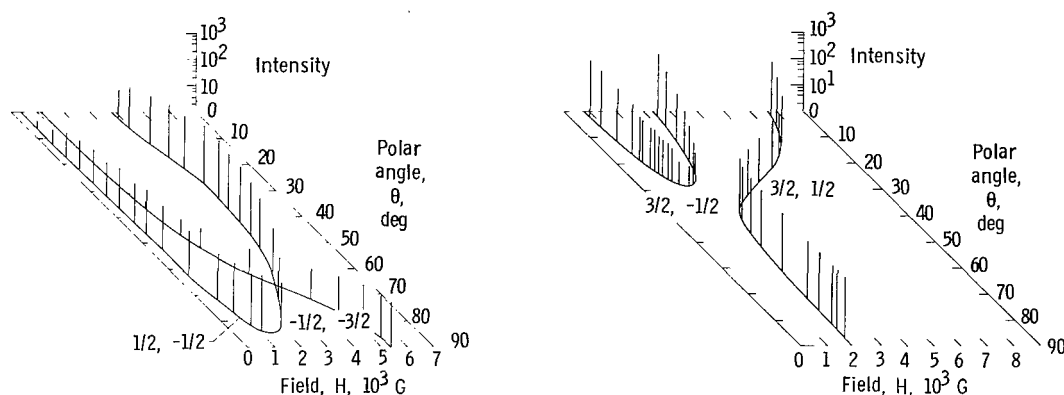


Figure 1. - Quasi-three-dimensional mapping of resonance fields and intensities for ruby Cr^{+3} fine-structure as function of polar angle between field and c-axis of crystal. Excitation energy, 9.543 gigahertz. Data presented in two graphs for clarity.

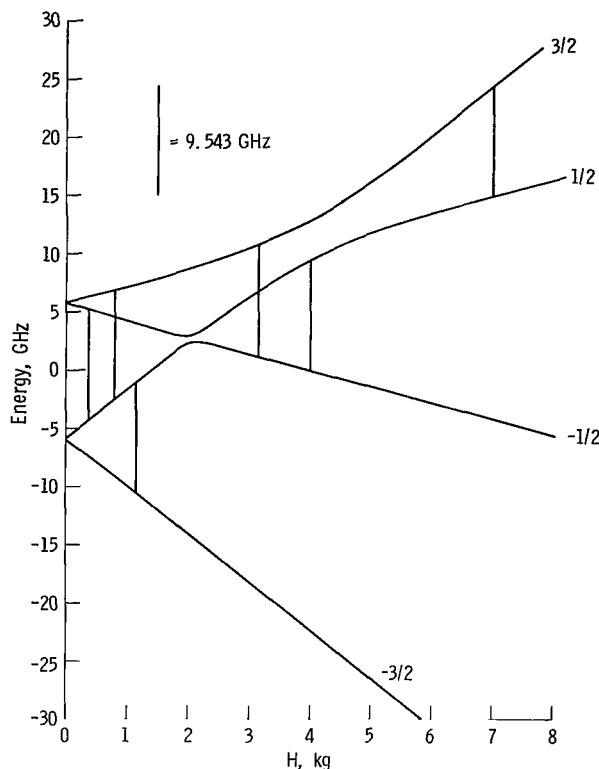


Figure 2. - Energy levels of Cr^{+3} in ruby against applied magnetic field. Polar angle between field and c-axis of the crystal, 10° . (Data taken from ref. 8.)

as a function of applied magnetic field for $\theta = 10^\circ$. As shown, six lines are possible with 9.543-gigahertz excitation. Their positions agree well with our observation as recorded in figure 1. The relative intensities of the various lines shown in figure 1 were obtained by a direct comparison of the line heights and widths of the first-derivative spectra.

X-ray Irradiation

In our study of the X-ray irradiation effect on ruby, it was experimentally expedient to place the sample in the microwave cavity with the c-axis always normal to the applied magnetic field. The samples would thus be isotropic with respect to rotations around the c-axis as well as the magnetic field. With such defined geometry, samples show two Cr^{+3} resonance lines at 1967 ± 2 ($g = 3.467 \pm 0.004$) and 5387 ± 18 ($g = 1.265 \pm 0.04$) gauss, corresponding to the $3/2 \leftrightarrow 1/2$ and $-1/2 \leftrightarrow -3/2$ transitions, respectively (see $\theta = 90^\circ$, fig. 1). The values given are the average values of random measurements through a

360° rotation of the crystal about its axis. The assigned precisions represent the range of extreme anisotropy due to a slight deviation of the c-axis of the crystal from a perfectly perpendicular position to the applied field.

X-ray irradiation of the samples was carried out at room temperature using a commercial unit operated at 40 kilovolts with a 15-milliampere tube current. The X-ray tube had a tungsten target and was equipped with a beryllium window. The decrease in Cr^{+3} relative concentration was measured using the dual-cavity technique. The saturation behavior with respect to the radiation was the same for both resonance lines, saturation being achieved at a total dose of about 10^6 roentgens. There was a 27-percent decrease in intensity for the 5387-gauss line but only 12 percent decrease for the 1967-gauss line. These results are shown in figure 3. We deem that results for the higher field line are

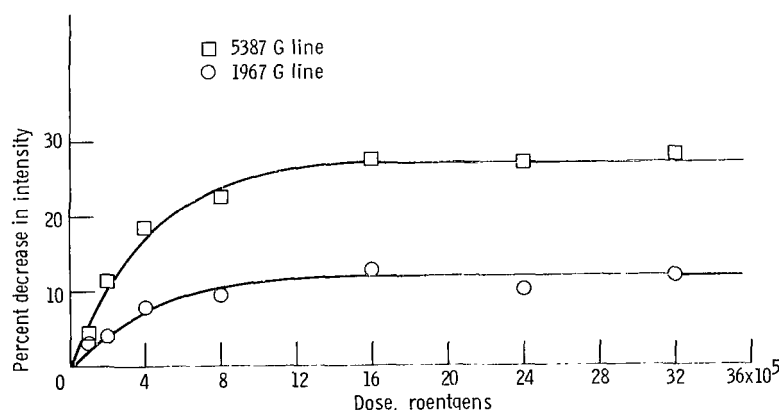


Figure 3. - Percent decrease in Cr^{+3} EPR intensity in X-ray irradiated ruby as function of dose.

more reliable. The lower field line might have been more affected by local random strain and crystalline field changes induced by the radiation.

Qualitatively, the irradiated sample had a bright orange color similar to that of $\alpha\text{-Al}_2\text{O}_3$ crystal containing chromium grown under conditions favoring the stabilization of Cr^{+4} ions (ref. 9). Furthermore, we noted no resonance line of g value of about 2 (which is normally associated with ordinary F centers, an electron trapped in an anion vacancy) to an upper limit of a few percent of the Cr^{+3} intensity.

Thermal annealing kinetics. - The annealing kinetics of the irradiated ruby crystal was studied by applying a technique similar to that used for the annealing kinetics of F centers in KCl (ref. 10). The method involved a dynamic measurement of the increase of Cr^{+3} concentration during an isothermal annealing. The EPR sample cavity was fitted with a set of Helmholtz coils which were programmed to sweep 180 gauss every 11.5 seconds, adding to the static field. During a thermal annealing measurement, the EPR

spectrometer was held at an applied field 90 gauss below the resonance field of the Cr^{+3} so that the adsorption line would appear at the middle of each sweep. The temperature of the sample cavity was raised at a predetermined constant rate, using a variable temperature controller coupled to a mechanical driver. The final annealing temperature was held constant to within $\pm 2^\circ \text{C}$.

The resonance intensity was observed as a function of time, which was equivalent to a function of temperature up to the time when the preset final temperature was reached. Figure 4 shows a typical set of the annealing data for the 5387-gauss line. The decrease

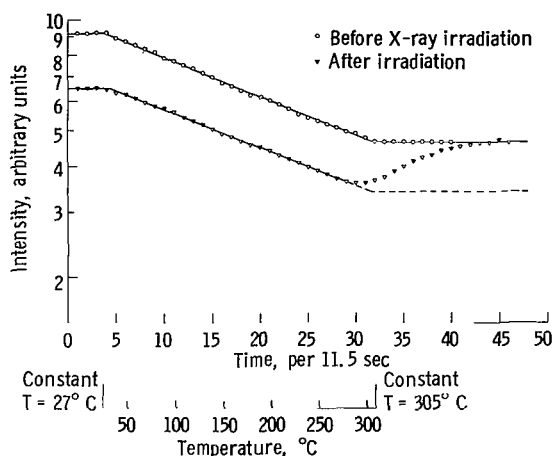


Figure 4. - Chromium⁺³ EPR intensity dependence on time and temperature.

in intensity from the start at room temperature to the end temperature at 305°C is due to the inverse dependence on temperature of the spin-state population difference, on which the EPR signal intensity depends. This is evident in the heating data of a sample before it was subjected to X-ray radiation. The post-irradiation annealing data of that sample initially shows the same rate of intensity increase. This shows that there was no optical annealing due to ambient light and that thermal annealing was not occurring at that temperature region. Near 305°C , thermal annealing begins to occur, and hence the intensity increases at constant temperature due to the chromium ions returning to their $+3$ state. Subsequent reheating of the annealed sample, after first cooling to room temperature, gives a set of data identical with that of the sample before irradiation. This indicates that the thermal destruction of the X-ray produced centers is complete. The data in figure 4 also show a 26.6-percent recovery in Cr^{+3} concentration, which agrees

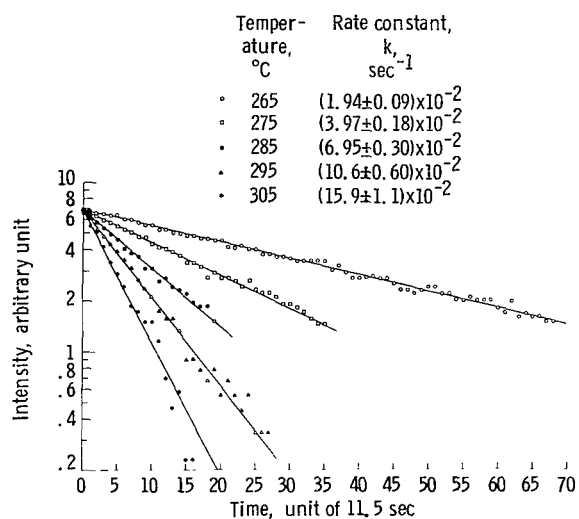


Figure 5. - Isothermal decay of radiation-modified chromium ions as calculated from observed Cr^{+3} EPR intensity for five specified temperatures from 265° to 305° C.

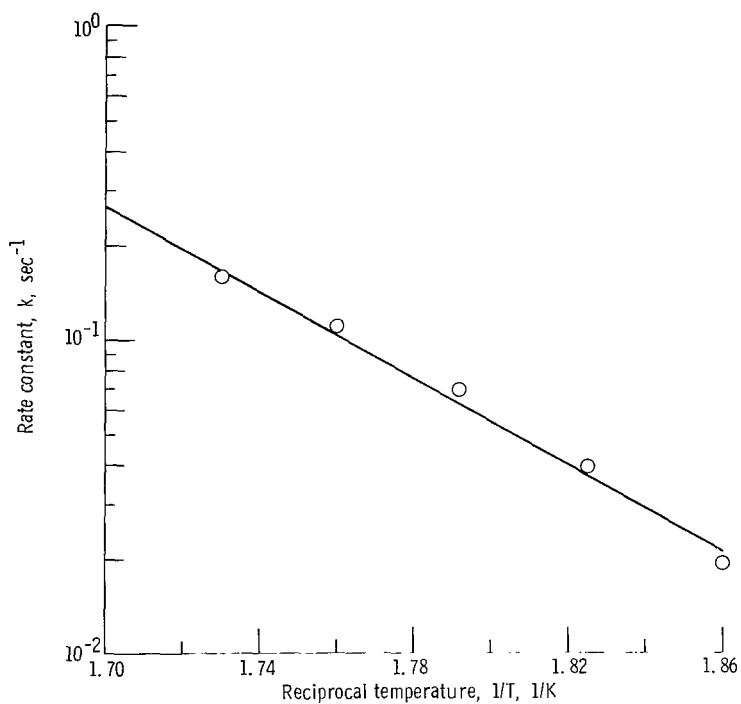


Figure 6. - Arrhenius plot of rate constant k as function of temperature. Line drawn is expressed by $\ln k = (-1.5850 \times 10^4)/T - 25.5962$, resulting from a least squares fitting of the experimental data.

well with the percent of Cr^{+3} loss determined by the dual-cavity measurements immediately after irradiation.

In figure 5, the logarithm of the radiation-modified chromium-ion intensity (Cr^{+3} intensity at infinite time minus Cr^{+3} intensity at time t) is plotted as a function of time for five isothermal anneals taken in the temperature range 265° to 305° C. The straightness of the lines indicates that the decay is exponential; that is, the kinetics is first order. The instrumentation error is assumed to be negligible. The uncertainty in the k 's listed in figure 5 represents an estimate of the extreme of the range in a straight-line fitting of the data points. An activation energy of 1.37 ± 0.07 electron volts was calculated, using a least squares fitting of the data points in a logarithmic plot of k against reciprocal temperature. The Arrhenius plot is presented in figure 6.

DISCUSSION

Several authors (refs. 2 to 4) have proposed that γ - and X-ray irradiation of ruby would raise an electron from the ground state of the Cr^{+3} into the conduction band; the electron may be subsequently captured by another Cr^{+3} to form Cr^{+2} . Thus, two centers are created, one which can capture an electron and another a hole. From glow curve studies, Arkhengelskii, Morgenshtern, and Neustruev (ref. 2) observed a second-order kinetics for the thermal destruction of the centers and determined the associated level depth to be 1.47 ± 0.02 electron volts. Although trap depth measurements from glow curves are valid, it is usually difficult to deduce kinetics from glow curves (ref. 11). Moreover, in their case, the glow curves were distorted by the presence of a quenching process.

The conclusion reached in this work is that the thermal recovery of Cr^{+3} is a first-order process. A first-order kinetics is tested by a good fit of the experimental data to the form $C = C_0 \cdot e^{-kt}$, where k is the rate constant and C and C_0 are the concentration of the reactant at time t and time zero, respectively; that is, a plot of $\ln C$ versus t should be linear with a slope of $-k$. We have shown in figure 5 that this is clearly the case for five separate samples measured at five temperatures, each of which is a good fit for a first-order kinetics. This suggests that either the activation of a hole or an electron from its center is the rate controlling process responsible for the recovery of the radiation-modified chromium ions back to their $+3$ state. It is not possible to conclude here which one it is, but one of the two must dominate unless the level depth of both the hole and the electron traps are by unlikely chance essentially the same. Our

results also show a quantitative agreement between the Cr^{+3} concentration loss by X-ray irradiation and that recovered by subsequent thermal annealing, that is, the radiation damage is reversible by heating.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 12, 1970,
129-03.

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